

Study of Li⁺ Ion-exchanger Mg₂TiO₄

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Abstract. Spinel-type metal oxides, magnesium-titanium oxide (Mg₂TiO₄), was prepared by a solid state reaction crystallization method. The spinel construction of Mg₂TiO₄ was conformed by XRD. The results showed that the Li⁺ extraction/insertion be progressed mainly by an ion-exchange mechanism. The acid treated samples had an ion exchange capacity of 13.9mmol/g for Li⁺.

Introduction

The inorganic ion-exchange preparation has the advantage of thermo-stability and radiation resistance, synthesis simple and good selectivity etc. In addition, it appears the fine speciality in dealing with nuclear waste, gathering and separating of metal ions and chromatogram analysis[1-2]. In this paper, inorganic ion exchanger (Mg₂TiO₄) with a spinel structure ion memory was synthesized by a solid state reaction crystallization method., which is different the reported in the literatures[3-5], and its ion-exchange properties were studied.

Experimental Section

Reagent and Instruments. MgO and TiO₂ were all analytical reagents; pure ethanol; D/max-A type X-ray diffraction instrument; Dx-170 type ion chromatogram instrument; XQM planetary ball mill; AA-670 atom absorption spectrum instrument; tubular-furnace.

Synthesis and Identifiable of Mg₂TiO₄. The pure ethanol was dropped into a XQM planetary ball mill mixed powder of MgO and TiO₂ with a Mg/Ti mole ration of 2:1 at the condition of constant rate churning. After 8 hours, the mixture was mixed completely. After mixing fully, the mixture was pressed to tablet by tablet press machine. Then the tablet was heat-treated for 4.5h at 900°C to obtain the Mg-Ti metal compound, the sample was designed as MgTi-900, whose theoretical formula was Mg₂TiO₄. Then it was analysed of x-ray diffraction and compared to literature[3-4].

Composition analysis: A 0.2g portion of sample was dissolved with acid. The Mg and Ti contents were determined by atomic absorption spectrometry.

The Cation Extraction of Mg-Ti metal compound and Acid Modification. Four 0.200g portions of sample (MgTi-900 compound) were immersed in a HNO₃ solution (50ml) of 0.01M, 0.1M, 1M and 10M respectively with shaking in constant temperature water at 25°C. After 3 days, take the supernatant solution to determine the cation concentration, test its acid proof ability and the extraction ration of Ti⁴⁺.

A 5g portion of sample (MgTi-900) was immersed in a 1M HNO₃ solution (500mL) with intermittent shaking in constant temperature water at 25°C. After 7 days, remove the supernatant solution and add new HNO₃ solution. Repeating that for twice, then the initial sample was transformed to H-type sample, washed with water and air-dried. The sample obtained by thermal crystallized at 900°C and acid modified was designated as MgTi-900 (H).

Saturation Capacity of Exchange. Weigh five 0.5g portions of MgTi-900 (H), then each portion was immersed in a 0.1M solution (10mL), containing Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺ respectively, diluted to 100mL, shaken in constant temperature water at 25°C. After saturation exchanging (namely, after 10 days by literature[3-4]) the solutions were filtered by subminiature aperture sieve, and the cation concentration was determined. At the same time, do vacant experiment. Last, the

inorganic exchanger saturation capacity of exchange for alkali-metal-ions obtained by decrease quantity.

Distribution Coefficient (Kd). After weighing four 0.100g portions of MgTi-900 (H), each portion of sample was immersed in a 0.05M mixed solution (0.200mL) containing Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ (Cl^-/OH^- ratios are different in each solution, $\text{C}(\text{Cl}^-)+\text{C}(\text{OH}^-)=0.1\text{M}$, $\text{C}=\text{Li}^+$, Na^+ , K^+ , Rb^+ and Cs^+). The alkali-metals ions total concentration all was $1.0\times 10^{-3}\text{M}$ by adding 9mL distilled water. After the samples were shaken for 7 days in constant temperature water at 25°C and were filtered, cation concentrations in each samples were obtained.

Results and Discussion

Compound and Appraisalment of Mg_2TiO_4 . The X-ray diffraction pattern of compound metal oxide (Mg_2TiO_4), crystallized was shown in figure 1. The structure of compound metal oxide Mg_2TiO_4 crystallized at 900°C was much perfect.

We know from chemical analysis, the composition of MgTi-900 is $\text{Mg}_{1.97}\text{Ti}_{0.99}\text{O}_{3.96}$, whose chemical component is basically corresponded with the composition of spinel-type metal oxides.

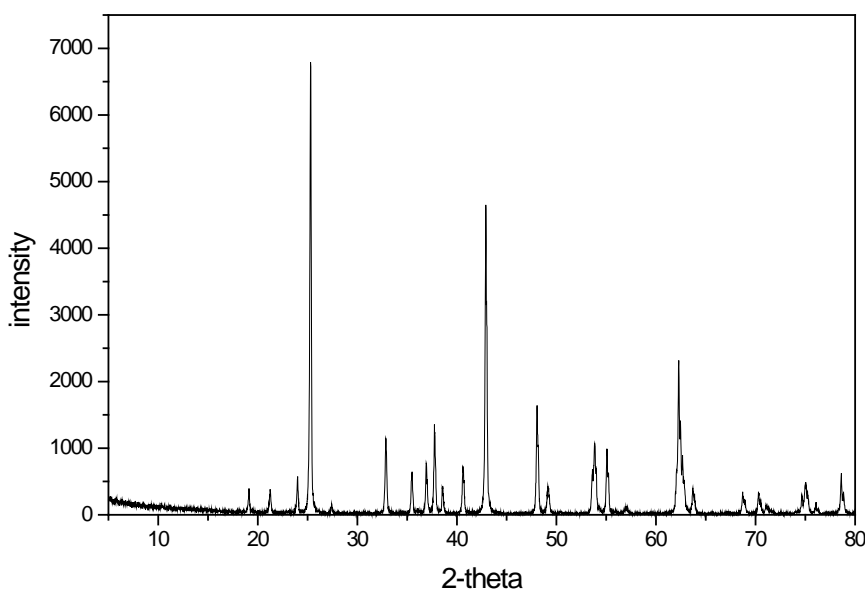


Fig.1 The powder's X-ray figures of $\text{Mg}_{1.97}\text{Ti}_{0.99}\text{O}_{3.96}$ crystal

Cation Extraction of Metal Compound Mg-Ti and Acid Modification. The extraction ration of Mg^{2+} and Ti^{4+} from MgTi-900 in different concentration HNO_3 solution is shown in Figure2. we know from Figure2, the extractabilities of Mg^{2+} are 35%~78% and Ti^{4+} are 2.4%~8.0%. Those indicate that the extractabilities of Mg^{2+} are higher than those of Ti^{4+} when exchanger was immersed in 1M acid solution, corresponding with the exchanger condition was better.(1 N, Mg^{2+} 73%, Ti^{4+} 6.1%)

X-ray diffraction of MgTi-900 (H), which is the acid modification product, is shown in Figure1. As shown, the structure of MgTi-900(H) is nearly constant, which is spinel oxide type too. It indicate that the exchanger is steady. The analysis indicate the composition of MgTi-900 (H) was $\text{H}_{2.87}\text{Mg}_{1.53}\text{Ti}_{0.93}\text{O}_{3.64}$, whose component of 73% Mg^{2+} transformed to H^+ compared with the composition $\text{Mg}_{1.97}\text{Ti}_{0.99}\text{O}_{3.96}$ before acid-treated. Then the specific Mg^{2+} of exchanger were extracted fulfill basically and remained the H-type identified with initial type.

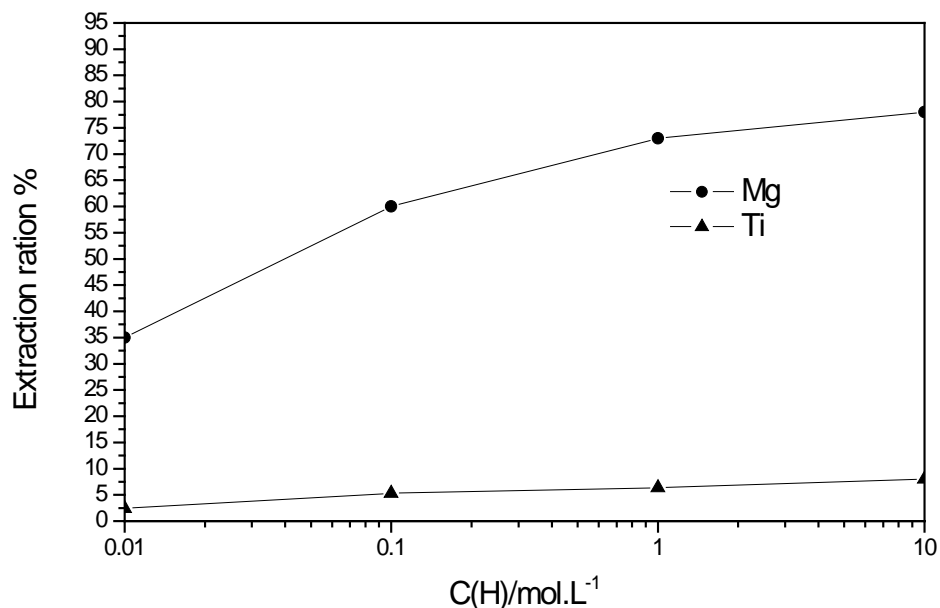


Fig.2 Extraction ratio of cations from MgTi-900 in nitric acid solution

Saturation Capacity of Exchange. The relation between radius and saturated ion exchange capacity of MgTi-900 (H) for alkali was shown in figure 3. Known from figure 3, the capacity of exchange for Li^+ was much higher than those for other alkali ions. The capacity for Li^+ is $13.9 \text{ mmol} \cdot \text{g}^{-1}$. It proved that the ion exchange synthesized has higher capacity of exchange, and better remembering of exchange for Li^+ . The effect factors of saturation capacity of exchange of MgTi-900 (H) are: 1) The Li^+ in exchange solution must be removed previously, because Li^+ exchanged with exchanger vacancy site when existing too much Li^+ ; 2) The experimental results shown that the exchange capacity of ion exchanger for Li^+ is much higher than those for other alkali ions in thin solution, which indicate that the ion-exchange reaction is carried out between and bare ions; 3) At the time of exchange, a Li^+ was replaced by one H^+ . Li^+ not only entered the vacancy site but also exchanged with the H^+ of surface. Therefore, MgMnTi-900 (H) has a higher exchange capacity for Li^+ .

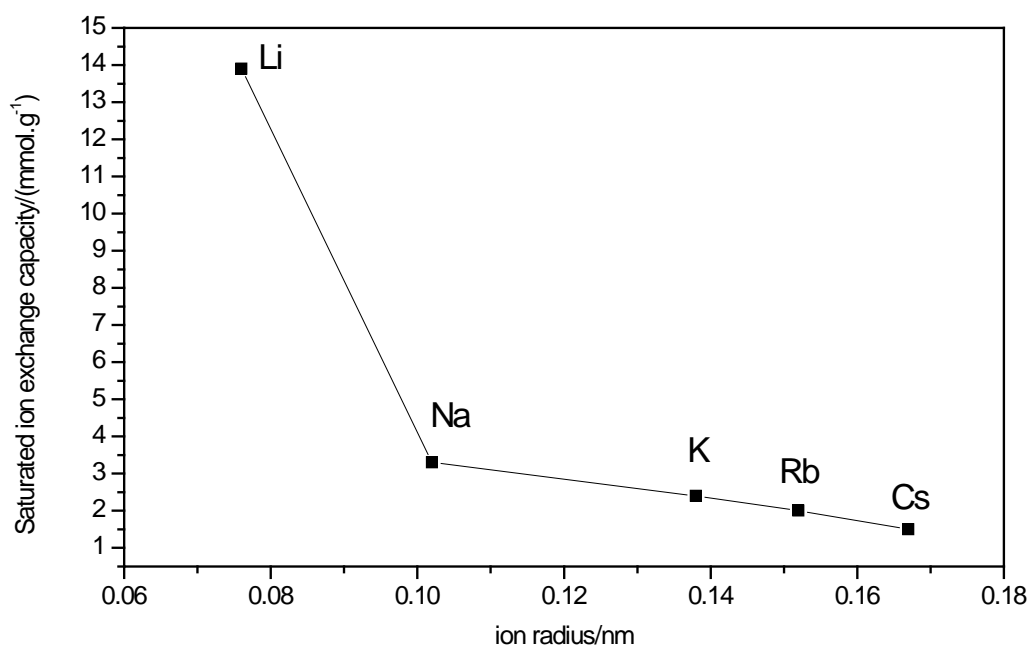


Fig.3 Relation between ion radius and saturated ion exchange capacity of MgTi-900 for alkali ions

Distribution coefficient(Kd). Kd values can be the token of exchange selectivity of MgTi-900 (H) for correlate ions. Shown in figure 4, Kd values of MgTi-900 (H) for alkali ions are larger and larger with an increase pH over the pH region studied. The selectivity sequence of MgTi-900 for alkali metal ions as follows:

$$Li^+ > Cs^+ > Rb^+ > K^+ > Na^+ \quad (1)$$

It indicates that MgTi-900 (H) has a better ion selectivity for Li^+ . Ion-exchange reaction is reversible reaction. The reaction of H^+ in ion-exchanger with alkali metal ions in solution as follows(example for Li^+):

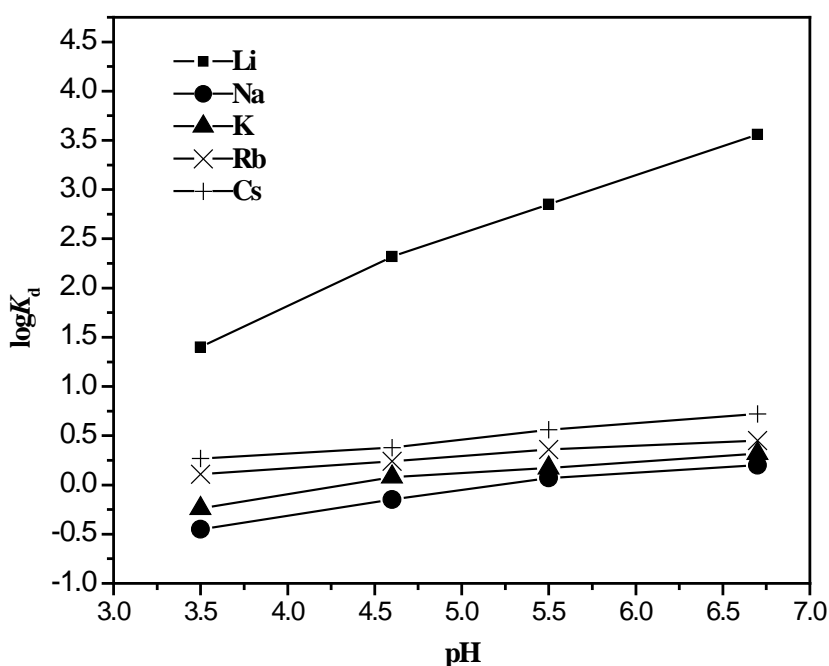
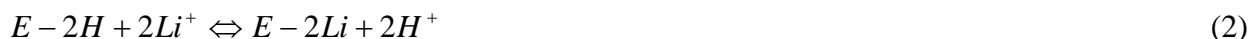


Fig.4 Distribution coefficient of MgTi-900(H)for alkali ions

Conclusions

The Mg_2TiO_4 of spinel-type metal oxide show a capacity extraction/insertion of Li^+ in the aqueous phase, by X-ray, saturation capacity of exchange and Kd measurement, etc. It has high selectivity to Li^+ . The Li^+ -extracted samples show a high selectivity and a large capacity for Li^+ among alkali metal ions.

Acknowledgments

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